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Influence of alkali ions on the efficiency of shrinkage reduction by polypropylene glycol in alkali activated systems

Lukas Kalina
Senior researcher, Faculty of Chemistry, Materials Research Centre, Brno, Czech Republic (corresponding author: kalina@fch.vut.cz) (Orcid:0000-0001-8127-8175)

Vlastimil Bilek Jr
Junior researcher, Faculty of Chemistry, Materials Research Centre, Brno, Czech Republic (Orcid:0000-0003-3831-3443)

Radoslav Novotny
Junior researcher, Faculty of Chemistry, Materials Research Centre, Brno, Czech Republic (Orcid:0000-0002-1809-5875)

Alkali-activated materials, especially when activated by water glass, exhibit substantial drying shrinkage that hinders their broader industrial application. The effect of shrinkage-reducing admixtures (SRA), based on polypropylene glycol, on drying shrinkage of alkali-activated blast furnace slag (BFS) mortars was examined. The determination of SRA efficiency and the influence of potassium alkali activators with varying silicate modulus on drying shrinkage characteristics were studied. It was observed that a high amount of alkalis positively affected the effect of SRA. The higher the amount of alkalis was, the lower was the drying shrinkage. The paper further discusses and underlines the role of the amount of alkali ions on the properties of alkali-activated BFS systems.

Introduction

High energy consumption and increased emissions along with ageing infrastructure have a harmful impact on the environment. Every year the production of concrete exceeds 10^{10} t, which is more than all other man-made materials combined. Such a huge production results in approximately 5% of the world's total anthropogenic greenhouse gas emissions (Damtoft *et al.*, 2008). Nowadays, this fact brings an even greater need to develop more environmentally friendly materials, which are more durable, highly recyclable and energy efficient.

Alkali-activated materials (AAMs) have become the materials of interest mainly owing to their low environmental impact compared to Portland cement and also because of the possibility of using varieties of industrial waste (Kalina *et al.*, 2012). The utilisation of AAM as an alternative binder instead of ordinary Portland cement (OPC) adds sustainability to concrete by reducing the carbon dioxide (CO_2) emissions compared to cement production. Many scientific studies have revealed that some kinds of AAM are distinguished by superior durability and lower heat of hydration compared to OPC binder, high resistance to aggressive environments (Hossain *et al.*, 2015) and good performance in high temperatures (Bernal *et al.*, 2015). Another advantage could be better behaviour under freeze–thaw cycles (Cai *et al.*, 2013). However, these materials exhibit drying and autogenous shrinkage (Bilek *et al.*, 2016), the subsequent formation of microcracks and higher formation of salt efflorescence, which are the major drawbacks that hinder these materials' broader industrial application.

Only a few authors have studied possible ways of reducing the shrinkage, which could be carried out using shrinkage-reducing admixtures (SRAs), belonging to the group of surfactants. The effect of SRA has been well investigated in Portland cement systems (Sant *et al.*, 2010); however, only little attention was dedicated to the study of efficiency of SRAs in alkali-activated slag (AAS) systems. It was concluded that the decrease in the surface tension of pore solution caused by SRA brought about smaller internal stress when the water evaporated. This resulted in the capillary stress being much lower than without the admixture. In terms of the drying shrinkage, the content of mesopores also plays a crucial role. According the capillary pressure theory (Bentz *et al.*, 1995), the system with a higher content of mesopores exhibits higher drying shrinkage (Collins and Sanjayan, 2000). The presence of SRA causes pore size redistribution (Palacios and Puertas, 2007), meaning that SRA decreases the percentage of mesopores in the total porosity of AAMs.

The SRA efficiency is entirely influenced by the nature of the electrolyte solution in which the SRA is located (Bauduin *et al.*, 2004; Morini *et al.*, 2005). There are two effects that have to be taken into account. The 'salting-in' effect initiates the solubilisation or miscibility of the surfactant in an aqueous electrolyte solution. By contrast, the 'salting-out' effect causes a decrease of the critical micelle concentration (CMC), increases the liquid–liquid miscibility gap and enhances the self-organisation. The question is whether the salting-in or the salting-out effect dominates in AAM. A high content of alkali ions in the system would imply that, for the AAM, salting-in may occur. However, the amount and the kind of cations in the pore solution significantly impact the surfactant's behaviour, as the Hofmeister or the lyotropic series suggest (Kunz *et al.*, 2004). To sum up, the present investigation is therefore focused on the role of specific alkali activators with different amounts of alkali ions influencing the shrinkage evolution and other properties of alkali-activated

blast furnace slag (BFS) systems with and without specific SRA based on polypropylene glycol.

Experiment

Materials

The aluminosilicate material used for the alkali activation was BFS from ArcelorMittal Ostrava, Inc., Czech Republic, with a specific surface area of 400 m^2/kg. The chemical composition specified by X-ray fluorescence spectroscopy (XRF) is shown in Table 1. The crystalline composition of BFS determined by X-ray diffraction (XRD) confirmed the presence of merwinite, melilite, β-C_2S and calcite. The BFS was activated by potassium water glass (Vodni sklo, Inc.) with defined silicate moduli: $M_s = 1{\cdot}92$ (4%); 1·29 (6%); 0·97 (8%); 0·78 (10%). The silicate moduli (silicon dioxide to potassium oxide (SiO_2/K_2O) molar ratio) correspond to the weight of potassium oxide in the activator, recalculated to the amount of BFS, as is shown in brackets. Three different fractions of standard siliceous sand (ČSN EN 196-1) were used for mortar preparation. The surfactant serving as the SRA was polypropylene glycol (PPG 425) with a specific molar weight, $M_w = 425$ (Sigma Aldrich, Ltd.). The amount of PPG 425 added into the alkali-activated mixture was determined as 0·5 wt%, recalculated to the amount of BFS.

Methods

Pore solution characterisation

The pore solutions were extracted from samples activated by water glass with different silicate moduli after 24 h using the hydraulic press BS-3000 (manufactured by BetonSystem company). After 24 h, the chemical composition of the pore solution did not change substantially and this time also indicates the beginning of drying shrinkage measurement. One hundred microlitres of pore solution were placed into a 100 ml volumetric flask and filled with water. The samples were then analysed by inductively coupled plasma optical emission spectrometry Horiba Ultima 2 (Horiba Scientific). The concentrations obtained were then used for synthetic preparation of pore solutions, which were further used for the surface tension measurement.

Surface tension testing

The surface tension of prepared samples was measured by the tensiometer BPA-800P (KSV Instruments) using the maximum bubble pressure method. The measurement was carried out in standard mode under the laboratory temperature (21°C). The pore solution was weighed out into plastic flasks, one containing the reference sample and the others containing PPG 425 in the mass concentrations of 0·05, 0·10, 0·25, 0·50, 1·00 and 2·00 wt% related to the mass of BFS, the amount of which corresponded to the amount of activator used that was necessary for alkali activation.

Drying shrinkage measurement

The mortar specimens were prepared according to ČSN EN 196-1 (ČSN, 2016) standard with the dimensions of $25 \times 25 \times 285$ mm and were subjected to the drying shrinkage tests according to ASTM C596 (ASTM, 2017b). After 24 h the specimens were removed from molds and kept in the n humidity chamber at approximately 50% RH until the age of 28 d. During this period, the relative length changes were measured almost every workday at the beginning and then usually every 3 d using the ASTM C490 (ASTM, 2017a) dilatometer.

Isothermal calorimetry measurement

All calorimetric measurements were performed using TAMAir isothermal conduction calorimeter by TA Instruments at the temperature of 25°C. For each measurement, 4 g of BFS and adequate amount of alkali activator were used. Slag was placed into 15 ml glass flask and alkali activator was dosed into admix vial. BFS and the activator were inserted into the calorimeter and tempered separately (for approximately 3 h), then mixed together and stirred for 2 min with a teflon stirrer. A siliceous sand was used as a reference sample. The amount of reference was chosen so that it had similar heat capacity as the sample, in this case being 15·5 g of reference.

Compressive strength testing

For the compressive strength measurement, the testing mortar samples with the diameters of $40 \times 40 \times 160$ mm were prepared according to ČSN EN 196-1 standard. Each value in compressive strength development was supported by the average of four measurements. The tests were performed at the ages of 24 h, 7 d and 28 d after the specimen preparation. The press BS-300 (BetonSystem) was used for the compressive strength measurement.

Results and discussion

First, the most suitable PPG 425 concentration for the test of drying shrinkage was determined. The dependence of surface tension of pore solutions on PPG 425 concentration is represented in Figure 1. Each pore solution extracted from samples activated by water glass of specific silicate moduli contained a

Table 1. Chemical composition of BFS according to XRF

	Chemical composition: wt%									
Raw material	Silicon dioxide (SiO_2)	Aluminium oxide (Al_2O_3)	Calcium oxide (CaO)	Sodium oxide (Na_2O)	Potassium oxide (K_2O)	Magnesium oxide (MgO)	Sulfur trioxide (SO_3)	Iron (III) oxide (Fe_2O_3)	Titanium dioxide (TiO_2)	Manganese oxide (MnO)
BFS	34·7	9·1	41·1	0·4	0·9	10·5	1·4	0·3	1·0	0·6

different amount of potassium ions. Even a small addition of surfactant led to a steep drop of surface tension. This effect was also supported by the presence of alkalis. Generally, the more alkalis that were present in the solution, the lower was the surface tension, and thus they positively influenced the effect of admixture. This is in a good agreement with the Hofmeister series and salting-in effect. This dependence was observed for all pore solutions. Nevertheless, the surface tension values of pore solutions with $M_s = 0{\cdot}78$ and 0·97 were basically the same within the deviation values. It can also be concluded that after a sudden decrease of surface tension the values did not change further but, on the contrary, they remained more or less constant for almost all solutions. This phenomenon occurred at the moment when the concentration of PPG 425 was 0·5 wt%, meaning that the surfactant reached its critical micelle concentration (CMC) (45–55 mJ/m^2). As a consequence, it was concluded that 0·5 wt % of PPG 425 should have been further added to the samples for the following measurements.

The efficiency of PPG 425 on the drying shrinkage development of potassium alkali-activated mortars is shown in Figure 2. The dependence of the drying shrinkage decrease on decreasing silicate modulus of the alkali activator is evident. This phenomenon is probably related to the formation of different amounts of calcium silicate hydrate (C–S–H) gel. A higher amount of C–S–H gel causes a more compact structure, which leads to lower evaporation of water from the capillary menisci (Figure 3) and, therefore, the drying shrinkage is consequently smaller. Nevertheless, within the same silicate modulus of alkali activator, higher weight losses of mortars with PPG 425 were observed, compared to those without it. This could be explained by the lower liquid saturation induced by SRA as previously described (Aïtcin and Flatt, 2015). Moreover, the amount of alkalis has a significant influence on drying shrinkage. Comparing the samples with PPG 425 and the reference samples, the effect of added surfactant is evident. Thanks to the higher content of alkaline ions, the efficiency of PPG 425 increases. It is obvious that the samples activated by water glass with low silicate modulus (0·78; 0·97) show a greater difference between the reference and the surfactant-containing samples in drying shrinkage evolution. This phenomenon is in a good agreement with previous results presented in Figure 1 and confirms the importance of the amount of alkali ions for the PPG 425 efficiency affecting the reduction of surface tension of the pore solution and the drying shrinkage.

The hydration mechanism was studied based on the calorimetry measurement. Figure 4 presents slag pastes activated by

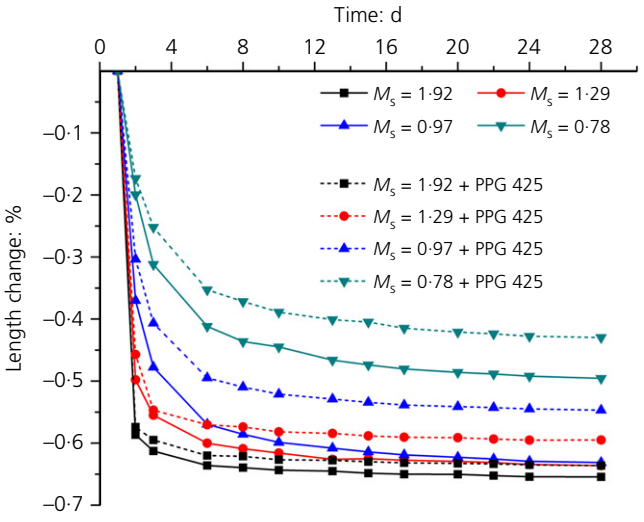

Figure 2. Effect of PPG 425 on drying shrinkage evolution of samples activated by potassium water glass with different silicate moduli

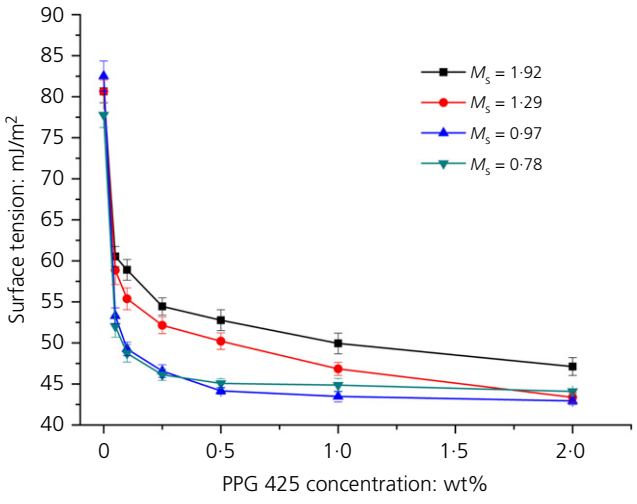

Figure 1. Surface tension of pore solutions with different silicate moduli of potassium water glass depending on the PPG 425 concentration

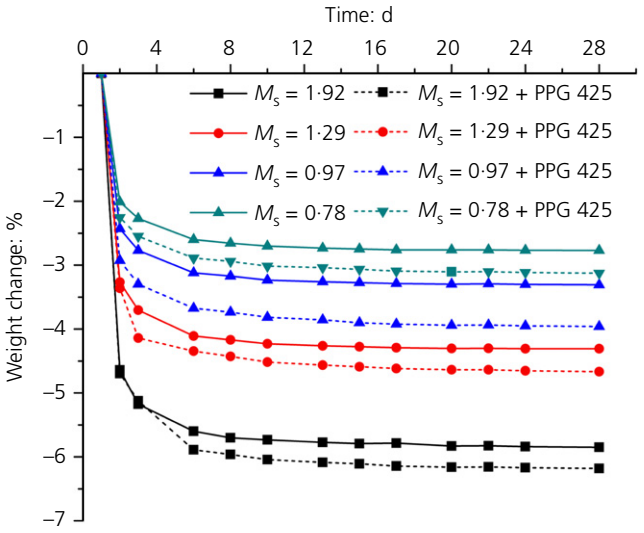

Figure 3. Effect of PPG 425 on weight changes of samples activated by potassium water glass with different silicate moduli

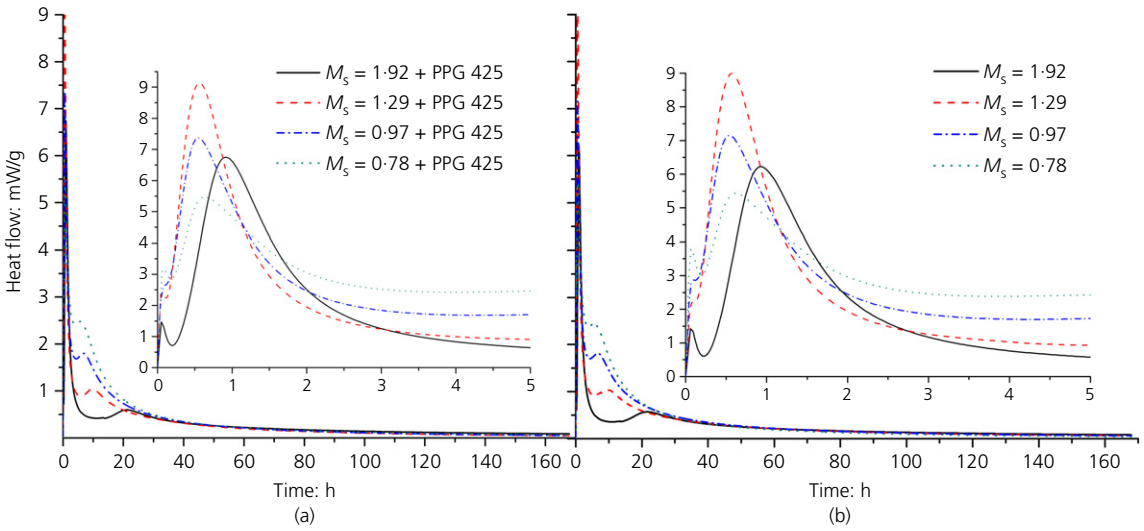

Figure 4. Heat evolution rate of slag pastes activated by potassium water glass with different silicate moduli: (a) with the addition of PPG 425 and (b) without it

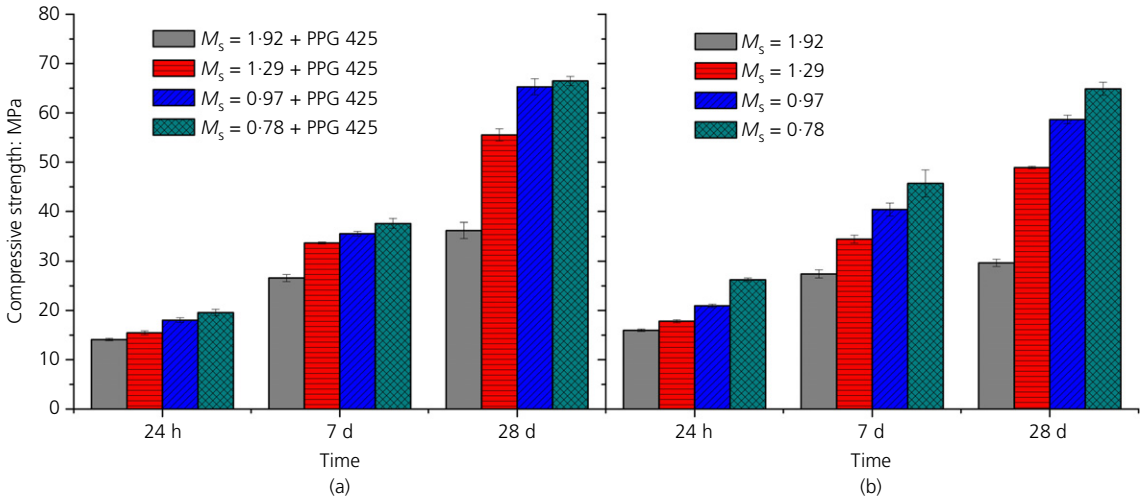

Figure 5. Effect of PPG 425 on the compressive strength development of samples activated by potassium water glass with different silicate moduli: (a) with the addition of PPG 425 and (b) without it

potassium water glass with varying silicate moduli (M_s = 1·92, 1·29, 0·97, 0·78). Figure 4(a) shows the heat flow evolution for the mixtures with added PPG 425, whereas Figure 4(b) demonstrates the curves for the mixtures without it. The amount of PPG 425 was always 0·5 wt% of BFS. Particular peaks capture various stages of the slag activation process. The first initial peak is always associated with particle wetting and slag dissolution and the second additional peak corresponds to primary C–S–H gel formation, both during the so-called pre-induction period (Shi and Day, 1995). Then the process is followed by the precipitation of the secondary C–S–H gel, and therefore the third peak was recorded. It was observed that the heat flow evolution remained the same for the mixtures with PPG 425 as well as without it. However, it was found that the samples activated by potassium water glass with various silicate moduli differed significantly in the third peak. Higher silicate modulus caused the delay of secondary C–S–H gel formation, and moreover decreased its heat flow release, which influenced the compressive strength development. When the mortars activated by potassium water glass were prepared, it was confirmed that the compressive strength was higher with decreasing value of silicate modulus of alkali activator (Figure 5). This trend is evident both in the samples with the addition of PPG 425 (Figure 5(a)) and in the reference samples (Figure 5(b)). The results are consistent with the calorimetry measurement, where it was proved that the samples activated by water glass with higher silicate modulus showed less formation of binder phase. It is also obvious that the addition of surfactant influences the compressive strength

development. In the early stages of the alkali activation process (1–7 d), the compressive strength of samples with PPG 425 is lower compared to the reference samples. After 1 d, the compressive strength of samples with PPG 425 achieved only 87% of the reference samples' values in cases of $M_s = 1{\cdot}92$, $1{\cdot}29$, $0{\cdot}97$ and just 75% for samples activated by potassium water glass with silicate modulus $M_s = 0{\cdot}78$. This decrease could be related to possible adsorption of surfactant to the BFS particles, which slows down the process of alkali activation, as previously described (Partyka *et al.*, 1984). After 7 d, the equalisation of compressive strengths of samples with surfactant and without it occurred, with respect to the error bars. However, the role of surfactant in preventing the drying shrinkage is visible after 28 d. The samples with PPG 425 did not show any visible cracks on their surface, which positively affected the compressive strengths results; see, for example, the samples activated by water glass with $M_s = 0{\cdot}78$. While the compressive strength of the reference sample between 7 and 28 d has been augmented by 30%, the strength of samples with PPG 425 added has improved by more than 40%. A similar trend was also observed in other cases.

Conclusions

On the basis of the results obtained, it can be stated that polypropylene glycol with the molecular weight 425 plays a critical role in drying shrinkage development. Its efficiency is highly enhanced by the amount of alkalis in the activator. The addition of the surfactant used slightly decreases the compressive strength in the early stages of the hydration process (1–7 d), but after 28 d it gives better results compared to samples without it. These pieces of knowledge point out the importance of using suitable SRAs to improve the properties of AAMs and consequently increase the potential for their broader industrial application.

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